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Molding of Oriented Short Fiber Composites

ultimate tensile properties

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MOLDING OF ORIENTED SHORT FIBER COMPOSITES
I. ULTIMATE TENSILE PROPERTIES

BY

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13. ABSTRACT

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Since the primary structural variables mentioned above cannot in practice be changed independently, the measured tensile strengths and ultimate elongations of molded specimens are correlated directly with the preparation techniques and processing conditions used in their fabrication. When some control is exerted over fiber orientation in flow moldings, it is found that voids, wetting, and dispersion are not critical. The study and implementation of controlled fiber orientation will be emphasized in subsequent reports of this series.

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II

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I. ULTIMATE TENSILE PROPERTIES

BY

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DECEMBER 1972

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FOREWORD

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Molding of Oriented Short-Fiber Composites
I. Ultimate Tensile Properties

by

Lloyd A. Goettler

- A B S T R A C T -

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V

INTRODUCTION

Injection and transfer molding afford an economical means to fabricate short fiber reinforced composites on a large volume basis. The hydrodynamic forces generated by the flow of the fiber-melt suspension alter the composite structure. The primary variables defining this structure are listed in Table 1; they directly determine the mechanical properties of the composite.

Material composition and processing conditions comprise a second group of variables; these are under the control of the fabricator (see table 2). But they can operate to change composite performance only through their effect on the primary structural variables. The relationship between these sets of variables is not straightforward, and at this stage remains heavily empirical. Moreover, one-to-one relationships do not exist between the members of each set.

This report describes the dependence of the structural parameters on the material and processing variables, and how they, in turn, influence the tensile strength and elongation of test pieces. The ultimate, rather than the elastic, properties are treated here because they are more sensitive to the structural variables. In Table 1, the term "wetting" includes resin penetration into fiber bundles and the existence of microvoids at the fiber/resin interface. These factors are under the influence of the processing conditions and participate in the determination of composite structure. Adhesion, on the other hand, is a physico-chemical phenomenon concerned with the strength of the fiber-resin bond and will not be considered.

Experiments were performed with an epoxy of the epichlorohydrin bisphenol-A type that was cured with methylene dianiline and reinforced with 1/4" or 1/8" E-glass fibers. The fabrication operation employed is termed plunger molding and comprises the flow of a fiber-reinforced polymer melt under the action of a plunger through a runner system into a closed mold cavity. Both a rod of 1/4" to 1/2" diameter and a 1/4" x 1" bar were molded through a 1/2" x 1/8" runner using various gates. A conventional end-gate of small cross-section used with the bar yielded a largely transverse orientation. In most of the experiments, the rod was preceded by a 6° conical converging section to enhance the fiber alignment along the rod axis. A detailed study of the orientation process used with this geometry is presented separately (1,2). Details of the materials, equipment, analyses, and geometry are given in (1) for the rod and (3) for the bar.

STRUCTURE OF A DISCONTINUOUS FIBER COMPOSITE

Three classes of composites can be differentiated according to the different levels of the structural variables in Figure 1. The primary distinction between these is the factor limiting the ultimate tensile properties. The optimal structure has long fibers that are well dispersed. Unfortunately, this combination is difficult to obtain with high performance reinforcements such as glass and graphite fiber, which are brittle. Moreover, long single fibers form a low density mass which is difficult both to handle and to impregnate, so the dispersion must be accomplished as part of the fabrication operation and is usually incomplete.

The one type of composite approaching this combination, listed as class II in the figure, is an impregnated fiber mat. However, even here it is usually small bundles rather than individual fibers that are dispersed, and the material is not amenable to economical flow fabrication.

Composites fabricated by flow molding and extrusion are consequently limited to well-dispersed short fibers (< 1/32") as in the fiberglass reinforced thermoplastics, or long (> 1/8") fibers in loose bundles. In the former case, class III, the good dispersion helps to gain back some of the properties lost by the short fiber length. This works reasonably well for certain thermoplastics which bond well to the fiber. But results are disappointing with thermosetting matrices. In a fiberglass/epoxy composite the tensile strength drops from 30,000 to 8,000 psi as fiber length is reduced from 1/4" to 1/16". In this work we must therefore be concerned with long fiber composites of class I. With the poor fiber dispersion, resin-rich fracture planes abound and composite performance is keyed to the orientation of these planes.

The oversimplified separation of variables indicated by Figure 1 is not to imply a complete isolation of effects. For example, fiber alignment in well-dispersed systems will enhance directional property levels, and fiber dispersion in the composites of longer aligned fibers will diminish the directional sensitivity by improving off-axis properties.

STRUCTURE DETERMINED BY PROCESSING

In the ensuing presentation, each of the six primary structural variables listed in Table 1 will first be treated separately. This will include methods of characterization and observation of change in that variable with variations in the more directly manipulated secondary variables of Table 2. The resulting effect upon composite strength will also be qualitatively described.

Since the primary structural variables can frequently not be changed independently, the measured tensile strengths of molded samples will later be correlated directly with the preparation techniques and processing conditions used in their fabrication. These affect one or more structural variables which, in turn, determine the mechanical properties. The major changes in structure and their effect on the properties will also be identified and discussed for each set of conditions.

Fiber Loading (concentration) .

Increases in tensile strength and modulus are generally observed at higher fiber loading. Some comparative data on transfer molded rods of the same orientation are presented in Table 3. Strength and modulus are both approximately proportional to the fiber concentration for these composites with an imperfect longitudinal fiber orientation. An exception to this rule is for moldings that are highly transverse. Such an orientation can be produced, for example, by molding through a small end gate.

Experimental data on epoxy moldings reinforced with 1/8" fiberglass show that a 20 v/o fiber content produces a transverse strength 25% higher than is obtained at 40 v/o.

The degree of variation in fiber concentration that occurs in a typical plunger molding through a gate is shown in Table 4. Rather than the expected fiber blockage of the gate accompanied by resin squeeze-through to produce a resin-rich front, the axial data suggest that the fibers on the average move faster than the resin. This is possible because they do not experience drag at the wall. The transverse measurements shown in the table indicate the presence of a lubricating layer of pure resin.

Wetting

In order to obtain a strong interface, it is necessary that the resin be in intimate contact with all fiber surfaces. The presence of dry areas between fibers in a bundle or of microvoids at the interface will preclude the establishment of adhesive forces. These can be varied according to the chemical coupling agent used, and will not be treated as a variable in this study.

Two forms of 1/8" chopped strand were used. Type CS308A (.524 mil diam.) supplied by Johns Manville consists of bundles containing 240 fiber ends and coated with an epoxy-compatible binder that incorporates a chemical coupling agent. This material was hand-blended as received into Epon 828 at 60°C immediately after activating it with methylene dianiline. The bundles retained their

integrity in this gentle blending process and tended to clump into grains which, after hardening to a B-stage at room temperature, could be easily handled. In the molding procedure they were electronically preheated in a LaRose r.f. oven and stuffed into the pot of the plunger molding machine. This material is termed the standard molding compound.

A second material consisted of the same fiber, except that the binding on the fibers was removed by heating in air at 400-600°C before incorporation in the epoxy. The fiber bundles still retained enough integrity to permit the hand blending operation described previously, but significant debundling occurred during flow in the mold. One percent of γ-aminopropyltriethoxysilane (A-1100) coupling agent was added to the epoxy resin before blending with the fibers. With the bundle coating burned off, a better penetration of the low-viscosity resin into the bundle was possible.

Since in both cases the same chemical systems were not used, differences in the exposed lengths and resin coverage of fibers in the tensile fracture surfaces of test samples molded from these materials (Figure 2) could be interpreted either as the effects of wetting or adhesion. However, polished cross-sections of the molding compounds indicate a low degree of resin penetration into the fiber bundles of the as-received fiber.

A further infiltration of resin occurs under the pressure of the molding operation. An increase in the degree of B-stage of the molding compound feedstock increases the resin viscosity during molding, which should result in a decreased wet-out. Some comparative scanning electron micrographs in Figures 2b and 3 illustrate these effects for heat cleaned fiber. Good wetting is indicated in the photomicrographs by a thick resin film on short exposed fiber surfaces, the absence of pull-out holes and the adherence of the resin to the fiber base. Additional evidence that higher B-staged molding compounds do not flow well is the appearance of voids in Figure 3a.

When the fibers lie in the fracture surface, the resin will remain in the interstices between fibers with good bonding but will crumble out during the fracture and leave voids when it is poor (see Figure 4). Coating of the fibers is again a significant criterion.

There was no apparent effect of molding speed, gate size, or mold temperature on the degree of wetting. It should be noted that mold temperature relates simply to the resin viscosity only when fill time is considerably shorter than cure time, which was not the case here*. The ultimate tensile strength, σ_u, of molded rods was also independent of the first two variables mentioned above, as well as the viscosity of the fiber-melt suspension.

*The molding properties cited in this section (and elsewhere as noted) have been obtained with a special molding technique wherein flow occurs while the melt is subjected to a high pressure of several thousand psi. Such a condition would occur in practice in the parts of complex cavities above a constriction. Similar results pertaining to the elastic modulus and processing details are given in (1).

Orientation

When the degree of dispersion in aligned systems is low, groups of fibers at angles to the stress direction, θ, in excess of 10° do not fracture. Rather, an interfacial debonding occurs around the fiber bundle or grain. Long discontinuous fibers ($\ell \geq 1/8$") unfortunately tend to form bundles, as mentioned earlier, and interfacial failure is observed in all flow moldings of this type. Strengthening of the interface, as by improved wetting, dispersion, and adhesion, are of some benefit, particularly when alignment is poor (see sections on Mechanical Properties). But the large magnitude of strength variation with fiber angle shown for a molded rod in Figure 5 supports the contention that strength in these long-fibered systems is predominantly orientation-controlled.

A reduction of molded rod diameter from 1/2" to 1/4" should result in a higher flow alignment of the fibers, but in fact does not cause a sizable increase in either elastic modulus (1) or strength. For 1/2" rods, molded with flow under pressure at 40 v/o of 1/8" fiberglass, the uncorrected tensile strength is 17.7 ksi. It increases only to 19.9 ksi for 3/8" rods and 20.1 ksi for 1/4" rods. With 1/4" fiber (CS308A), the strength in the 1/2" rod is only 14.5 ksi, lower than with 1/8" fibers. The tangling, bending and intertwining of the larger 1/4" fibers causes them to have a lower orientability. However, in the 1/4" diameter rod, the orientation of the 1/4" fibers can be augmented by interaction with the wall, yielding

better alignment along the rod length and a considerably higher tensile strength of 31.1 ksi. The ultimate elongation in all cases is about 0.7%. Orientation effects are discussed more completely elsewhere (1,2).

Fiber Length

A complete characterization of the variable of fiber length must include determination of the distribution or frequency of occurrence of the entire spectrum of lengths in the composite. Because it is the volume fraction of reinforcement that defines the mechanical property levels of fiber-reinforced composites, this distribution must be weighted according to the volume occupied by each fiber length fraction. In the case of chopped strand, including both glass and graphite fiber, wherein the diameter of all segments are the same, the weighting may be done on a length rather than volume basis. Also, for this case, the aspect ratio distribution is identical to the fiber length distribution. The method of determining fiber length distribution is described in the Appendix.

Some examples of measured fiber length distributions are shown in Figures 6 and 7. F_v is the volume weighted probability density function. For example, 70% of the volume of fibers in the sample have a length that is less than that corresponding to $F_v = 0.7$. Note in Figure 6 for plunger-molded epoxy reinforced with 1/8" CS308A that very little fiber damage occurs when the fibers are used in their bundled condition. When

the binder is removed by heat treating at 600°C, the bundles open up and more fiber damage occurs. The fiber lengths used in thermoplastic molding compounds (Figure 7) are much smaller. However, little further damage results on passage through the screw of an injection molding machine. Table 5 gives a comparison of the median fiber lengths in different molding compounds.

Most fiber damage should occur in the contracting flows at small gates or the entrance to small channels rather than in flow through uniform channels themselves. The flow of highly concentrated suspensions is lubricated by shear through a thin layer of pure resin at the wall. Thus, the fiber mass is not highly sheared during flow in straight channels and only deforms in elongational flow fields. However, the same amount of fiber damage occurs with either 1/8" or 1/2" diameter upstream gates. The average fiber length is reduced by .25 mm. when one dimension of a rectangular gate is reduced as low as 1/32". There is no effect of flow rate up to 5 in^3/min or cavity pressure up to 1800 psi on the fiber length distribution.

Bundle integrity in the molding compound has been shown to be necessary to maintain a high fiber length and aspect ratio in the molded part. There is evidence to suggest that an even higher aspect ratio can be maintained when these bundles are thoroughly wet out. This prevents fiber fracture due to collapse of the bundle and deterioration from interfiber friction.

However, it is desirable to have the bundles open up during the flow molding process so that a better overlapped and more homogeneous fiber network is produced in the molded part. An example of how a decrease in fiber length can be compensated by an increase in wetting and dispersion of the fibers in repeated moldings is exhibited by the data of Lewis (5) in Table 6. Other experimental data linking the measured fiber lengths to tensile properties are discussed in the section on materials.

Fiber Dispersion

The degree of fiber dispersion can be measured by the spread in angles between close individual fibers in a molding. If these fibers were contained in a tight bundle, they would all lie in the same direction. As the bundle opens up, the fibers have a greater freedom to take up differing angular positions in the formation of a fiber network. This effect is evident in the series of photomicrographs presented in Figure 8. The standard deviation of the distribution of angular positions of individual fibers lying within a 0.01 inch diameter region on a planar surface cut into the molding is taken as a measure of dispersion. For the standard molding compound it is found to be as low as 10.7° at a high rate of fill exceeding 100 in^3/min, 13.5° at 30 in^3/min and 16.6° when the flow occurs while under a high compaction pressure.

The latter condition represents a high energy input during flow because the voids are collapsed and the highly concentrated suspension is forced to deform like a true liquid. If dispersion is postulated to increase with increased energy dissipation in the material, then it should increase with an increase in pressure drop for flow or should vary directly with the product of flow rate and viscosity. We notice, however, from the preceding paragraph, that the dispersion is lowest at the highest flow rate. Most likely, that is due very low level of viscosity that accompanies a high flow rate in our experiments.

In fact, it is noted in Figures 9a and 9b that for 1/4" fibers, the ultimate tensile elongation of molded rods increases at both high and low flow rates. A possible explanation for this behavior is the lower dispersion under those conditions. This has been observed visually in polished surfaces of the moldings. It is substantiated by the photographs in Figure 10 of the fiber residue in parts of moldings that had been ashed.

Dispersion of the fibers in the final molding is necessary for the attainment of high strengths when the fibers are not highly aligned in the direction of stress. It is necessary to avoid fracture through pure resin along a bundle or grain interface that is transverse or at an acute angle to the stress direction. These cleavage type fractures severely limit the strength of flow molded composites.

If the orientation is sufficiently good ($\theta \leq 10°$), the clumping or bundling of the fibers can be tolerated as long as the parallel filaments are overlapped. Long bundles of small diameter would be preferred because of the resulting high shear stress transfer to the fiber bundle, large distance between ends to yield a higher probability of overlapping, and a large number of bundles per fiber content. Since cracks appear along the fiber direction more consistently than around the ends of fiber bundles, however, it appears that the orientation of fibers is more critical in "oriented-fiber" composites than is the fiber end overlapping.

There is a rather poor dispersion in the standard molding compound. This is illustrated by the high bundle integrity shown in the first picture of the sequence in Figure 8, which is located at the entrance to the runner system. The fiber bundles are just beginning to experience shear and elongational hydrodynamic forces. The progressive disintegration of the bundles occurs in the remainder of the sequence as the gate is approached along the 2-1/2" long runner. The correlation of angular spread with individual fiber dispersion should be noted.

At the low flow rate used for these photographs, the bundles are expanded, broken apart and intermeshed with nieghboring bundles even in the center of the channel, although more so near the walls where the shear is higher. Shear extends to the runner's center because of its small 1/8" thickness and because the cure advances to produce a high viscosity in the long time required to fill the cavity at low ram speed. At higher flow rates,

evidence of bundle disintegration and regions of shear are limited to the vicinity of the wall. Fiber damage would accompany the dispersion process and would occur in straight channels only when the matrix viscosity is high (> 10^4 poise) or the channel is very small.

Void Content

Three types of voids occur in composite materials. True voids in the resin (usually of a large size $\geq$ 100 μ) occur infrequently in epoxy systems which cure without the release of volatiles. They then must result either from too fast a fill in an improperly vented mold or too stiff a resin that cannot be properly compacted. Compaction would be especially hindered by inefficient pressure transfer through a pinched upstream region. These voids are not highly detrimental to composite strength if their concentration is below several volume percent.

A second type of void is of an elongated shape and results from incomplete welding together of strands, grains, or bundles of molding compound. Such a defect is extremely harmful to tensile strength if it lies normal to the stress direction. Unfortunately, this happens frequently in the molding of an elongated member, such as a bar or rod, through a small end gate.

The grains of molding compound are elongated in the flow through the runner and align into the direction of flow in passing through the narrow gate. On emerging from the gate into the larger cavity, either the individual fibrous strands must buckle or, if the melt is not compacted in the cavity, the entire extrudate may fold back on itself as the streamlines diverge and the flow decelerates to fill the larger cross-sectional area. In either case, local transverse weld lines will form that are, at best, pure resin, and may include voids. An example of such an occurrence in an unstressed sample is shown in Figure 11. These are sometimes referred to as transfer molding cracks.

The third type of void is a microvoid that results from incomplete wet-out of fiber bundles. It is illustrated in Figure 12. Because this type can also assume an elongated shape running the length of a drawn-out bundle, it may severely limit the ultimate tensile properties. Conditions leading to improved fiber wetting will tend to reduce this type of voidage.

Voidage may be measured by an areal analysis of finely polished surfaces cut into the molding or by determination of the density of the molding. The former method requires extremely careful handling to avoid the interference of polishing damage, and is not amenable to characterizing the small microvoids of type 3. Density measurements are straightforward, but calculation of the porosity requires precise values of the resin and fiber component densities and the fiber content in the composites. Errors in the derived porosity of $\pm$ .02 are not uncommon. Nevertheless, the simplicity of the method makes it attractive for comparative measurements.

By this method the void content of molded standard mix was found to be .048, irregardless of whether 1/2" or 1/8" diameter gating was used. This result appears high, but the densities of 1.20 and 2.54 gm/cm^3 used for the resin and glass respectively are known to yield high predictions of the porosity. When the B-stage and viscosity of the resin are very low, a void content of only 1.8% results. When a sigma blade blender is used to add shearing action in the compounding of the resin and glass, which opens up the fiber bundles for better resin infiltration, the void content in the molding drops as low as 1.3%. Since the porosity correlates with the fiber wetting, the voids in predominance must be those of type 3 discussed above.

The porosity was also measured in material located at the end of the converging section when the rod was partially filled by stopping the molding sequence abruptly at that point and curing the partially filled part. Because of the decreasing cross-sectional area in the flow direction, the material was partially compacted at this point. The porosity during flow in the region where the fiber orientation was being changed to produce an axial alignment varied from 9.% at a low flow rate of 2. in^3/min to 11.% at 65. in^3/min. This high voidage causes an anomalous dependence of fiber orientation on deformation rate under certain molding conditions (2).

The porosity data are summarized in Table 7.

MECHANICAL PROPERTIES CORRELATED WITH PROCESSING

Material variables and molding compound preparation.

The standard preparation technique for molding the epoxy compound using bundled E-glass (Johns Manville, type CS308A) was described previously in the section on fiber wetting. However, to improve the fiber dispersion and wetting of the fibers in the molding compound, the usual epoxy formulation was compounded with 1/8" bundled E-glass fibers (v_f = 0.40) in a mechanical sigma blade blender. This additional shearing broke apart the fiber bundles and allowed better resin penetration. During this step the resin was still uncured and the temperature was maintained at 60°C to permit high resin flowability. After B-staging, the material was plunger molded into the rod cavity through a conical converging channel.

The tensile properties of the molded rods appear in Table 8. With a 6° cone, the modulus of the presheared material is about 30% lower and the tensile strength 40% lower than that which is obtained from the standard molding compound. The increased fiber attrition that occurs when the protective bundles are dispersed is not sufficient to cause the observed decrease in stiffness, so that a poorer orientation is indicated. This is confirmed by visual observation of the orientation patterns in polished planes cut into the molded rods. The lower orientation level can also explain the reduced tensile strength.

When the convergence occurs at high elongation rates in the sharp right angle configuration, however, the tensile properties of both molding compounds are identical. Neither one orients to a high degree under these conditions. The elongation to failure of 0.6 to 0.7% is the same for both materials under all molding conditions shown in the table.

The heat-cleaned fiber described earlier also exhibits improved fiber dispersion and fiber wet-out, but these are accompanied by higher fiber damage in molding. In fact, these factors are all greater than with the presheared material because the complete removal of the bundle binder allows greater dispersion. Starting with the same 1/8" fiber, the volume-median aspect ratio of fibers in a typical plunger molding is only 141 for the heat-cleaned fiber, as compared with 204 when the fibers are used in their as-received condition. The improved wetting or adhesion over the standard molding compound has been exhibited in Figure 2. This, along with the greater fiber dispersion, results in a 25% increase in the transverse tensile strength of molded bars.

The heat cleaned fibers exhibit about the same degree of orientation as the standard material in the elongational flows that occur in filling the rod mold. Calculations of the predicted modulus according to the method of integrating over measured orientation profiles described in (4) show that the decrease in aspect ratio from 204 to 141 only decreases the modulus by 1% in a typical molded rod. Consequently, the rod modulus should then be a measure of the degree of fiber alignment. Comparisons with the standard molding compound are shown in Table 9. On the average, the moduli, and hence the orientation in the two materials molded under the same conditions, are the same, but the strength of the composites molded from heat-cleaned fiber are 28% low. It is possible that the fiber damage that occurs severely affects strength, offsetting the benefits of improved wetting and dispersion, whereas modulus is less sensitive to aspect ratio and is unaffected. This is substantiated by the less angular fracture pattern observed with the heat-cleaned fibers. Ultimate tensile elongation is .5-.6%.

Another method for obtaining greater fiber dispersity in a molding is through the use of fibers coated with a soft binder. The bundles can then be sheared apart more easily by the flow during mold filling. One such E-glass fiber (AeroRove II, by Glass Fiber Products Corp.) was used at a length of 1/4". Molding compounds of this material were prepared in the standard manner, and were molded into 1/2" diameter rods by a converging flow through the 6° cone. In this geometry, the fibers realign from a transverse position into the direction of flow. The resulting tensile properties and orientability parameter, λ, defined by (1)

$$\tan\theta_1/\tan\theta_1^\circ = (A/A^\circ)^{\frac{3}{2}} \qquad (1)$$

where

A/A° is the area ratio of the downstream and upstream cone cross-sections

are compared with the standard 1/4" fiber molding compound for slow fills in Table 10. It can be seen that all properties are essentially identical. A slight difference in fiber dispersion that is observed in polished sections of the moldings apparently does not have a significant effect at low flow rates.

However, as flow rate and elongation rate are increased, the properties do not go through a maximum as in the case of the more highly bundled materials (2). This may be due to the more homogeneous structure that results when the fibers disperse. At 30 in^3/min, which yields the optimum elongation rate for the standard CS308A in a 6° cone, the modulus and tensile strength are 17 and 25% low, respectively.

It should be noted that none of the properties are equal to those attainable with 1/8" fibers. The orientability of 1/4" fibers is low because they twist, bend, and interact to a higher degree than the shorter 1/8" fiber length.

Graphite fiber/epoxy molding compound (Fiberite Hy-E 1315-B) with a 1/4" fiber length was observed to orient to the same degree as 1/4" glass fiber. The orientation parameter, λ, was measured at 0.6. The tensile modulus of plunger molded 3/8" diameter rods was high (6. x 10^6 psi) but tensile strength was very low, with values less than 10,000 psi. Ultimate tensile elongation was only 0.2%. The nominal fiber content of this material is high at 60% by volume. Tensile strength probably suffers in such graphite composites because of high sensitivity to off-axis fiber bundles.

Processing conditions

Some processing variables that might possibly affect the strengths of plunger moldings are:

1. Amount of flash.
2. Amount of cushion (cull).
3. Degree of preheat or plasticization.
4. Pressure attained in melt during cycle.
   a. Maximum, or booster pressure
   b. Hold pressure
5. Time to fill the mold (fill rate).
6. Temperature of the mold.
7. Area of the gate.

Experiments were conducted to determine which of these are most significant. Some transfer moldings of a 1/4" x 1" x 6" end-gated bar were made with an epoxy/1/8" fiberglass molding compound containing approximately 40 v/o fibers. Tensile strength

was measured on an Instron testing machine and corrected to a value corresponding to a completely transverse orientation by integrating the equation of Ishai and Lavengood (6) over the measured orientation distribution. The effective transverse strength was then correlated against the above variables. For 54 molded specimens a multilinear regression analysis indicated that only three processing variables were important. These were: 1. Amount of flash, 4a. Maximum pressure, and 6. Mold temperature. Strength increased with increments in all of these. Only first-order effects were determined, as insufficient data were available to test for interactions.

A material parameter that was also varied was the degree of B-stage. This showed a definite effect, with the low B-stage being desirable. Transverse tensile strength increased from 2,000 psi to 5,000 psi as the % epoxide groups reacted in the B-stage was reduced from 55% to 45%.

The observation that excessive flash yields a stronger part is believed to result from the improved material flowability that would contribute to higher flash at a fixed pressure. Note that the degree of B-stage, also thought to be an important variable, is related to this same material behavior. Similarly, a higher mold temperature could cause a lower material viscosity on molding, allowing stronger weld lines, better wet-out of the fibers, better elimination of voids, etc. These same factors would be improved by the application of the higher molding pressure.

The tensile strength of molded rods with high longitudinal fiber alignment was also found to be a function of the maximum cavity pressure attained during the molding cycle, as shown in Figure 13. The increase in σ_u with P is attributed to improved resin infiltration and wet-out of the fibers. [Compare Figures 2b) and 3b) for changes of wetting with pressure.] The strength improvement may result either from the high pressure *per se*, or because high pressure levels are registered by the cavity pressure transducer only when the B-stage and resin viscosity are low. The strengths uncorrected and corrected for this pressure effect are plotted as a function of flow rate, Q, in Figures 14a and 14b. The sample standard deviation is reduced from 2.2 to 1.8 x 10^3 psi by this correction.

Summary and Conclusions

The results of the parametric study on transverse strength results may be generalized by concluding that stronger moldings are produced by enhancing the fiber wet-out. Consequently, low viscosity, low degree of reaction of thermosets during processing, high temperature, and high pressure are beneficial.

Greater fiber dispersion not only allows better wetting, but gives the molded composite a more homogeneous structure, so that off-axis cleavage cracks along fiber or bundle boundaries are not as prevalent. However, these benefits are important only when fibers are improperly aligned against the stress direction and are furthermore counteracted by the greater breakage of the individual

fibers that occurs during mold filling. This damage is not sufficient to affect stiffness, but causes a 30-40% reduction in tensile strength. Highly dispersed fibers orient as well as bundled ones but partial debundling yields a lower degree of uniaxial orientation except in very strong or weak elongational flows. Bundled fibers do not align as well under these conditions (2). The lower rotational mobility of a composite of partially bundled fibers can be rationalized by considering the rotational unit to be a loose collection of fibers that must rotate together. It exhibits a greater resistance to rotation than single fiber or tight bundles because of greater interaction with other units. In addition, it probably has a lower effective aspect ratio.

Very few fibers fracture in tensile tests of flow-molded short fiber composites. When the fiber length equals or exceeds 1/8", the fibers are bundled and interfacial failure along grain boundaries predominates. Shorter fibers of $\ell/d < 40$, even though more highly dispersed, cannot be shear loaded to failure and pull out of the matrix.

The ultimate tensile strength increases with fiber content when the fibers are aligned within about 30° of the stress direction. Samples that have a largely transverse fiber orientation exhibit the opposite effect. However, a higher fiber dispersion (loose bundles) allows a 25% increase in transverse tensile strength.

Tensile elongation is higher when the reinforcement is highly bundled. This occurs at both very high and very low fill rates, since under these conditions the work input in terms of deformational energy dissipation is lowest.

The general conclusion is that voids, wetting, and dispersion are not critical parameters in flow moldings when the fibers are properly aligned into the direction of highest stress. The fibers must be $\geq$ 1/8" to sustain high loads in the epoxy system studied. Then the tensile properties are largely determined by the degree of fiber alignment and the fiber content. When orientation is adverse, the other parameters become more critical.

Acknowledgment

The author wishes to express his gratitude to Mr. D. J. Morotz and to Miss A. M. Gordon for their assistance in the experimental phases of this study.

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Appendix

A determination of the fiber length distribution in a molded sample of a discontinuous fiber reinforced polymer is accomplished by the following steps:

i) Burn the resin away from the glass fibers contained within a large piece of the sample by heating in an air atmosphere for 45 min. to 1 hour.

ii) Gently pull a portion of fibers, which will be interlocked to some degree, from the center of the sample, making sure that no part is within a distance from a cut edge equal to the maximum fiber length in the sample.

iii) If the fibers are larger than 1/32" in length, a dispersion may be photographed at about 6 x magnification for the length measurement. For this purpose, the wad of fibers is dispersed in distilled water or a pure solvent in an ultrasonic bath to avoid further breakage. The entire sample is poured into a black (for glass) or white (for graphite fiber) enamelled tray. The fibers do not agglomerate if the tray is left undisturbed as the solvent evaporates.

iv) In the case of smaller fibers, the photograph for length measurement must be taken at 30-50 x magnification under a microscope. The fibers are dispersed in an ultrasonic bath, as above, but are then poured onto a microscope slide. The sides can be built up to avoid spillage. After the solvent

evaporates, glass fibers are photographed under dark field illumination. This yields a photograph of the dispersion with excellent contrast. A dispersion of graphite fibers could instead be collected on a piece of white filter paper and photographed under incident illumination.

In either of the above two steps it is necessary to make a quantitative transfer of the suspension of fibers in the dispersing solvent to the evaporating surface(s) in order to ensure a homogeneous sample. Each suspension may be divided onto more than one evaporation surface if it is ensured that all parts of all dispersions are photographed uniformly.

v) A border is drawn around the edge of each photograph to leave a margin equal in width to the longest fiber length. All fibers, part of which lie within the interior of the frame, must be measured for length. This measurement must be weighted according to the length of the fiber falling within the interior region. (This procedure assumes that all fibers have the same diameter. In the case of whiskers, for example, the width would have to be measured as well, and weighting would be according to the particle volume that falls inside of the framework.)

vi) The length measurements may be made from the photographs using a Zeiss particle size analyzer. With this device, which is pictured in Figure A-1, a variable-diameter light spot is centered on each fiber to be measured. Measurements are made by adjusting the spot size to just contain the fiber length and are automatically counted in a series of 48 registers. At the time of measurement, a hole is punched through the fiber to indicate that it has been counted.

vii) By using a large field in the photograph and drawing the border through the separations around large groups of fibers so that no fibers cross the border, the weighting length will equal the actual fiber length in all cases. Then only one series of measurements is required. However, one must be very careful not to bias the results when drawing the nonuniform margin around fibers. An example is shown in Figure A-2.

viii) At least 500, and preferably 1000, fibers should be measured for each material characterized. After tabulating the frequency of measurement for each length sector, the length-weighted length distribution can be calculated either by hand or, preferably, on a computer.

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   - PRESENCE OF VOLATILES
   - RESIN B-STAGE

TABLE 3

EFFECT OF FIBER CONTENT ON TENSILE PROPERTIES OF 1/8" GLASS FIBER/EPOXY COMPONENTS

FIBER CONTENT, V/O	YOUNG'S MODULUS, E X 10^{-6} PSI	ULTIMATE TENSILE STRENGTH, σ_u X 10^{-3} PSI
25	1.84	16.6
40	3.33	26.3

TABLE 4

VARIATION IN FIBER CONTENT

1/8" E-GLASS IN EPOXY

I. AXIAL	
MOLDING COMPOUND	41.6 v/o
GATE	44.7 v/o
MOLDING	49.7 v/o
II. TRANSVERSE	
CORE	43.9 v/o
OUTSIDE	41.6 v/o

TABLE 5

FIBER LENGTHS IN INJECTION AND TRANSFER MOLDINGS AND MOLDING COMPOUNDS

MATERIAL	FIBER CONTENT w/o	MEDIAN FIBER LENGTH, MM. MOLDING COMPOUND	AFTER MOLDING
EPOXY-WITH BINDER	60	3.1	3.0
-PRE-SHEARED IN SIGMA BLADE BLENDER	60	3.1	2.2
-HEAT TREATED	60	3.1	1.6
NYLON 66 (LNP COMPANY)	60	.23	.23
NYLON 6 (LNP)	60	.30	.23
POLYPROPYLENE (THERMOFIL)	40	.56	.49
PET(LNP)	40	.36	-
PET(LNP)	20	.43	-

TABLE 6

Fiber Damage in Ram Molding of a Graphite Fiber/Thermoplastic Molding Compound

Material	Passes through Molding Machine	Volume-median Aspect Ratio	Tensile strength, 10^3 psi
Thornel 50/ polycarbonate	0	1060	
	1	108	9.3
	2	42	10.5
	3	32	9.4
Courtaulds Type A/ Nylon 66	1	51	18.1
	2	34	18.0
	3	34	16.1

TABLE 7

VOID CONTENT

40 v/o 1/8" CS 308A IN EPOXY

DURING FILL	10 v/o

IN MOLDED PART:

HIGH VISCOSITY (10^4 POISE)	5 v/o
LOW VISCOSITY (500 POISE)	2 v/o
PRE-SHEARED	1 v/o

PARAMETER DEPENDENCE OF POROSITY

	VARIABLE	SIGN OF CORRELATION COEFF.
FLOW RATE	Q,	+
DEFORMATIONAL ENERGY DISSIPATION,	nQ	-
MAXIMUM MOLDING PRESSURE,	P	-

TABLE 8

TENSILE PROPERTIES OF RODS MOLDED FROM PRE-SHEARED EPOXY MOLDING COMPOUND

MATERIAL	ENTRANCE	ROD DIAMETER, D INCHES	FLOW AFTER COMPACTION, GRAMS	FLOW RATE Q $IN^3/MIN.$	E 10^6 PSI	σ_μ 10^3 PSI
PRE-SHEARED	6° CONE	1/4	6	NO EFFECT	2.0	12.8
		3/8	15	"	2.1	12.1
		3/8	0	5.5	2.4	13.3
STANDARD		1.4	6	NO EFFECT	2.8	20.1
		3/8	19	"	2.6	19.9
		3/8	0	5.5	3.6	27.1
PRE-SHEARED	SQUARE ENTRY	3/8	0	5.0	2.4	16.4
		3/8		24.0	1.9	9.8
STANDARD		3/8	0	5.0	2.3	17.5
		3/8		24.0	1.9	9.8

TABLE 9

PROPERTIES OF MOLDINGS MADE FROM HEAT-CLEANED FIBERS
$\alpha = 6°$ 40v/o 1/8" CS308A FIBER IN EPOXY

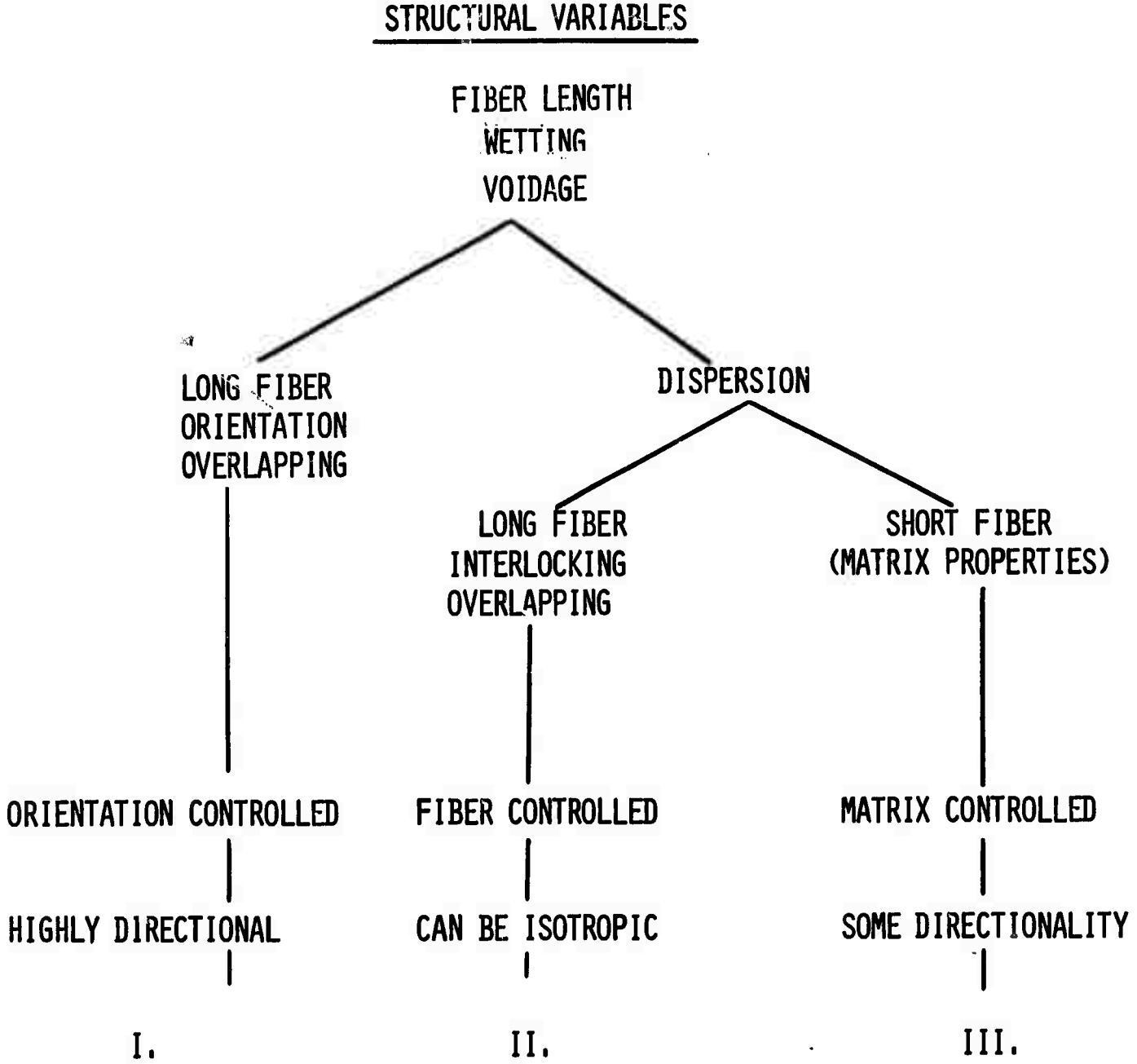
FIBER LENGTH, INCHES	ROD DIAMETER INCHES	FLOW AFTER COMPACTION, GRAMS	FLOW RATE IN^3/MIN	HEAT CLEANED FIBER E 10^6 PSI	HEAT CLEANED FIBER σ_μ 10^3 PSI	STANDARD FIBER E 10^6 PSI	STANDARD FIBER σ_μ 10^3 PSI	% DECREASE USING HEAT-CLEANED FIBER E	% DECREASE USING HEAT-CLEANED FIBER σ_μ
1/8	1/2	>10 GMS.	-	2.7	12.6	2.5	17.7	-8	29.
		0	2.5	2.5	-	2.3	-	-9.	-
			11.	2.6	15.3	3.0	19.5	13.	22.
	3/8	0	6.	3.1	14.1	3.6	27.5	14.	49.
1/4	1/2	>10 GMS.	-	2.5	13.1	2.3	14.5	-8.	10.
						AVG.		0	28.

TABLE 10

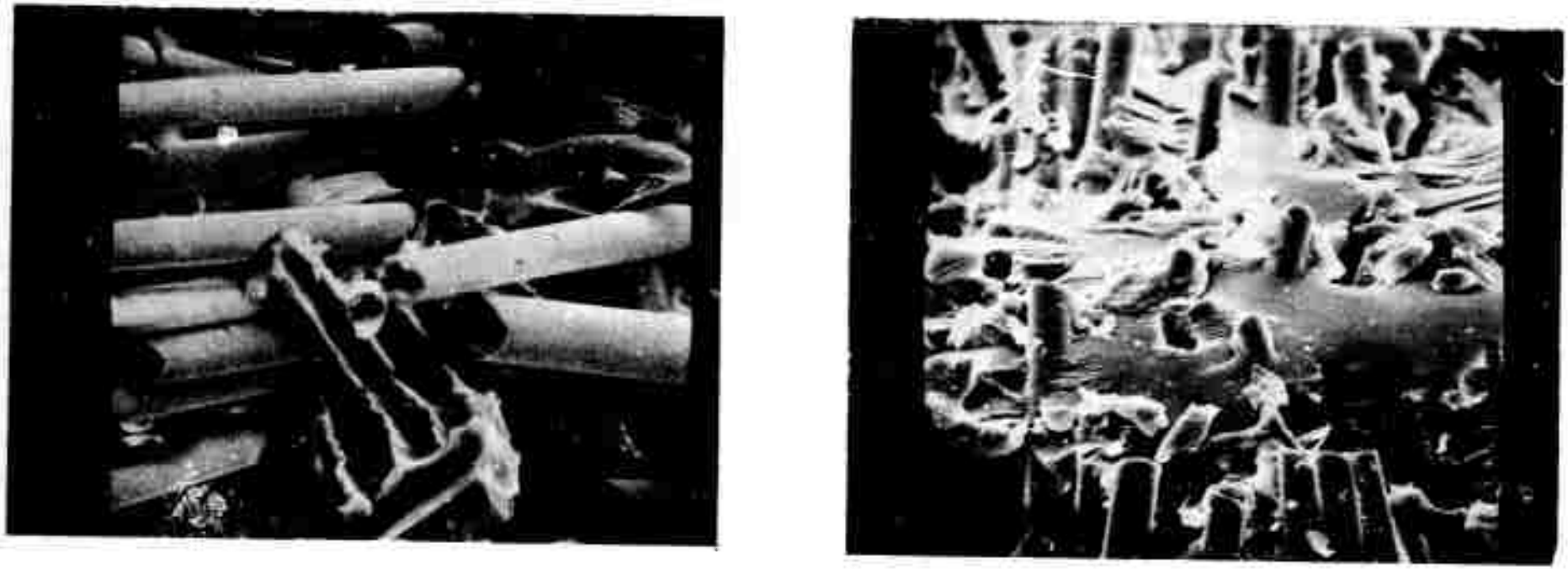
PROPERTIES OF MOLDINGS MADE FROM A FIBER WITH A SOFT BINDER

$a = 6°$ — No Flow After Compaction — 1/4" AeroRove II — 1/2" Diam. Rod.

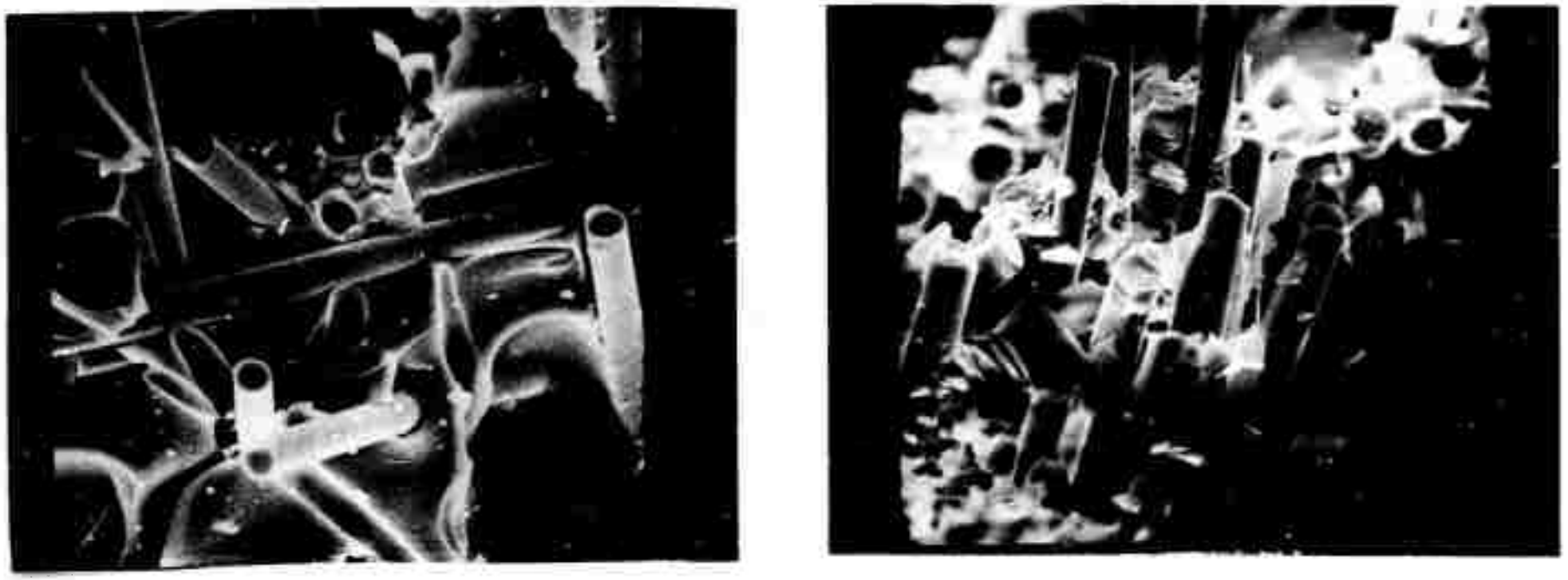
Q	λ		$E \times 10^{-6}$ PSI		$\sigma_u \times 10^{-3}$ PSI		ε
IN^3/MIN	AeroRove	CS308A	AeroRove	CS308A	AeroRove	CS308A	%
1.1	.84	.72	-	-	12.9	13.4	.7
4.0	.90	.85	2.0	2.3	12.1	14.6	.7



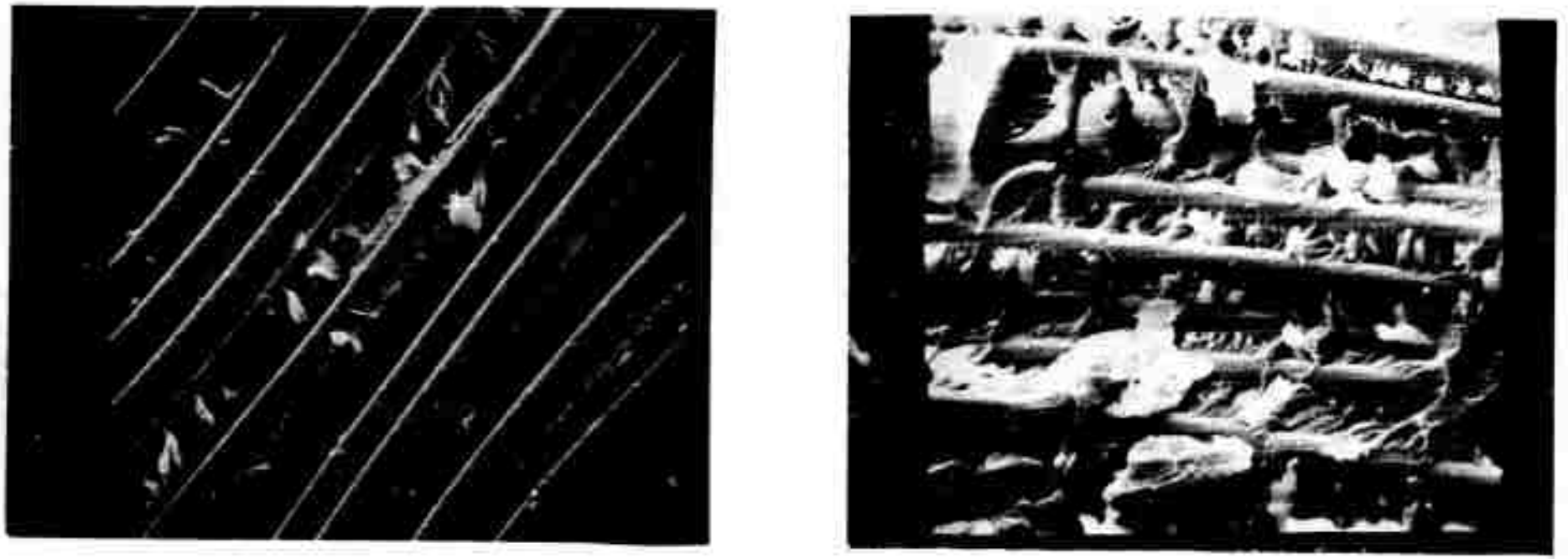
1. Types of discontinuous fiber composites related to structural variables.



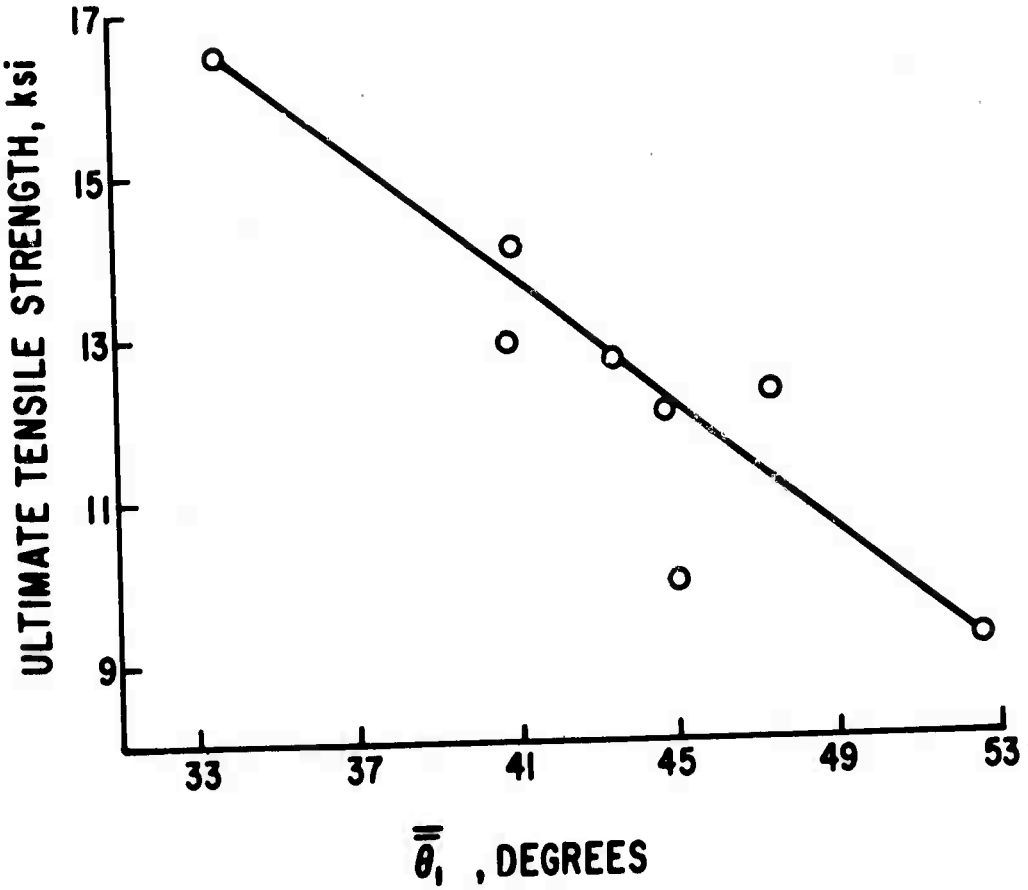
2. Scanning electron micrographs of epoxy composites made with a) as-received bundled and b) heat-cleaned fibers; 50% B-stage, 3,000 psi.



3. Scanning electron micrograph of epoxy/heat cleaned fibers: a) 57% B-stage, 3,000 psi; b) 50% B-stage, 1,600 psi.



4. Scanning electron micrographs of in-plane fractures; a) poor bonding; b) good bonding.



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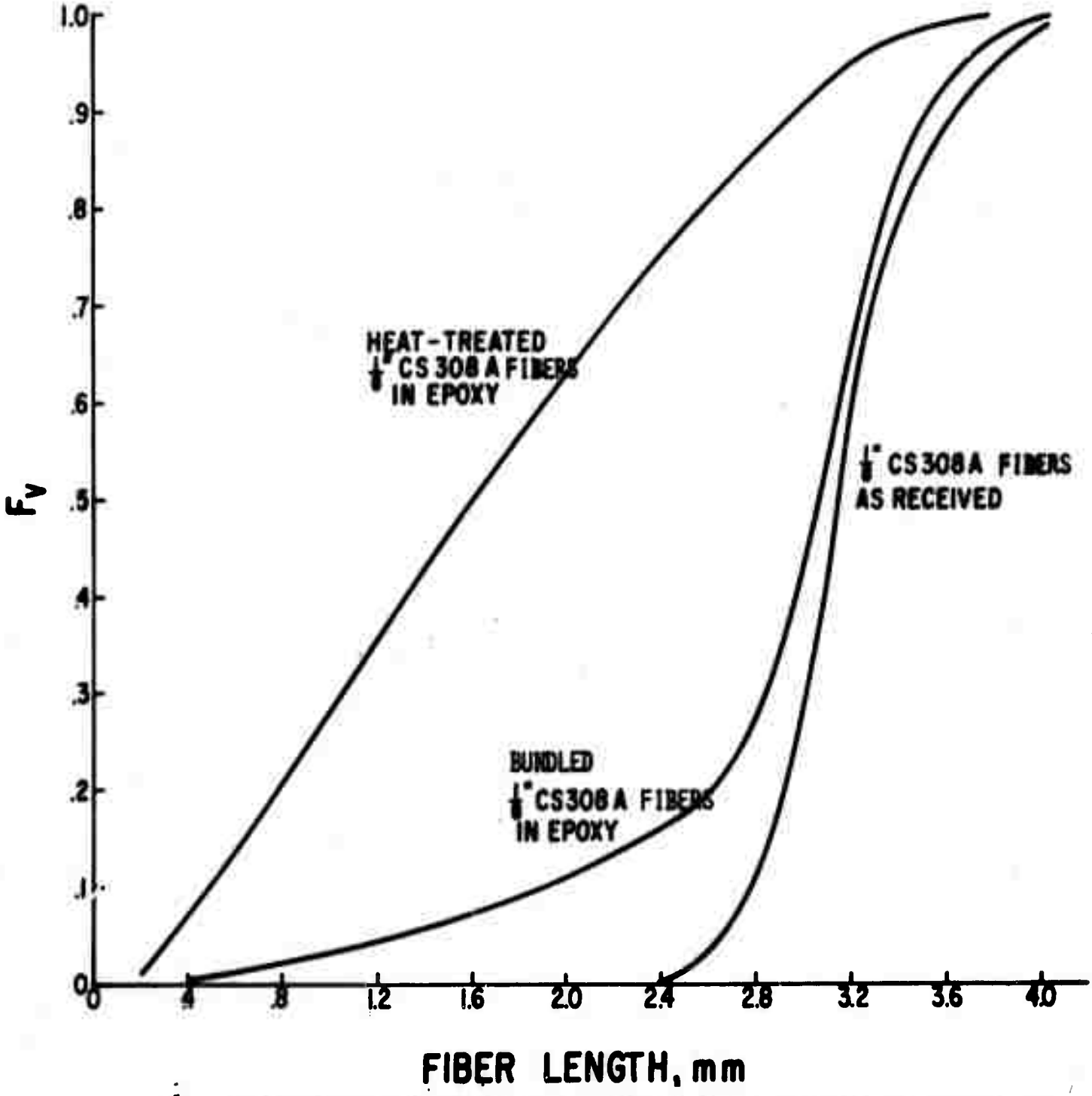
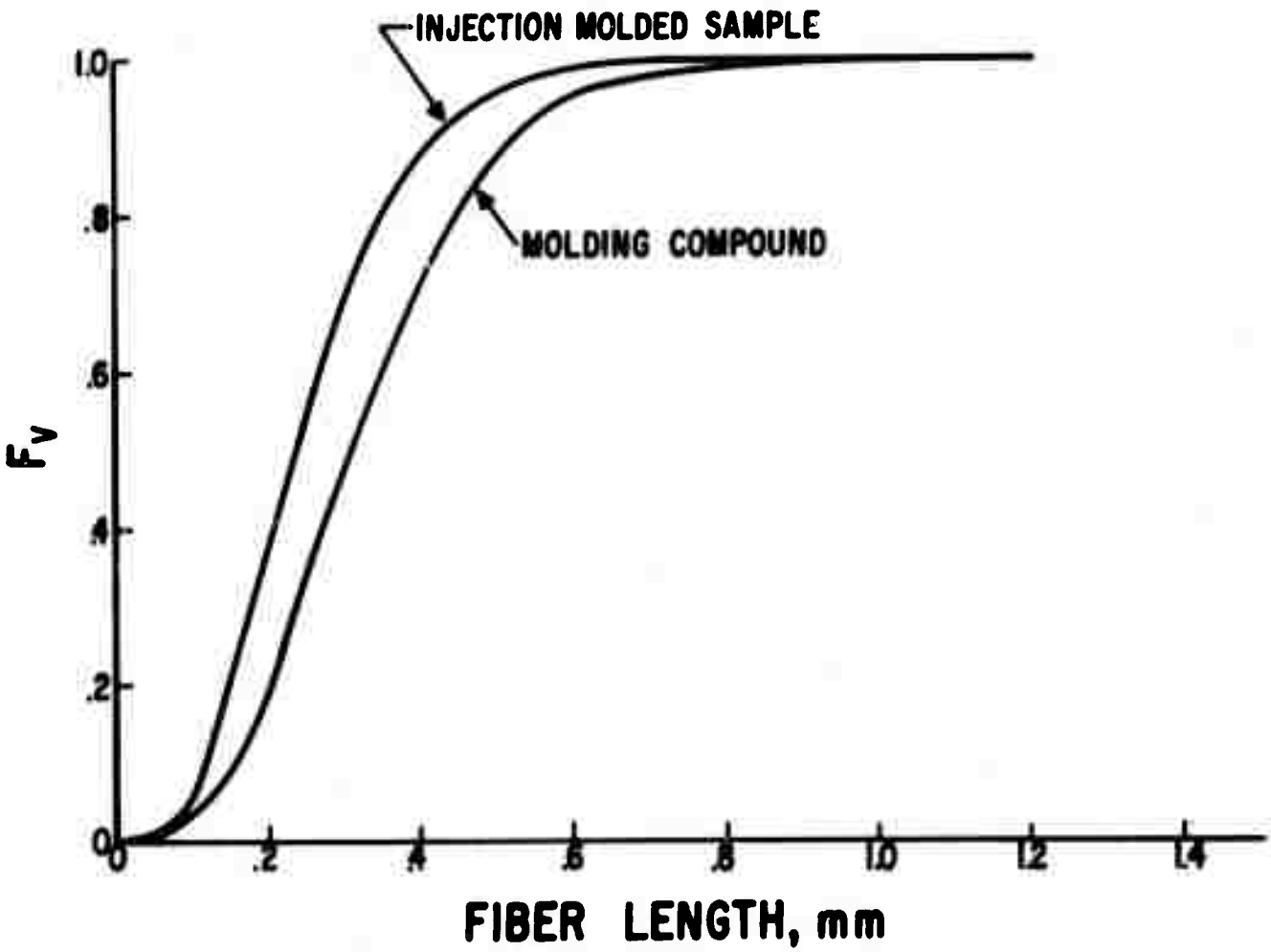
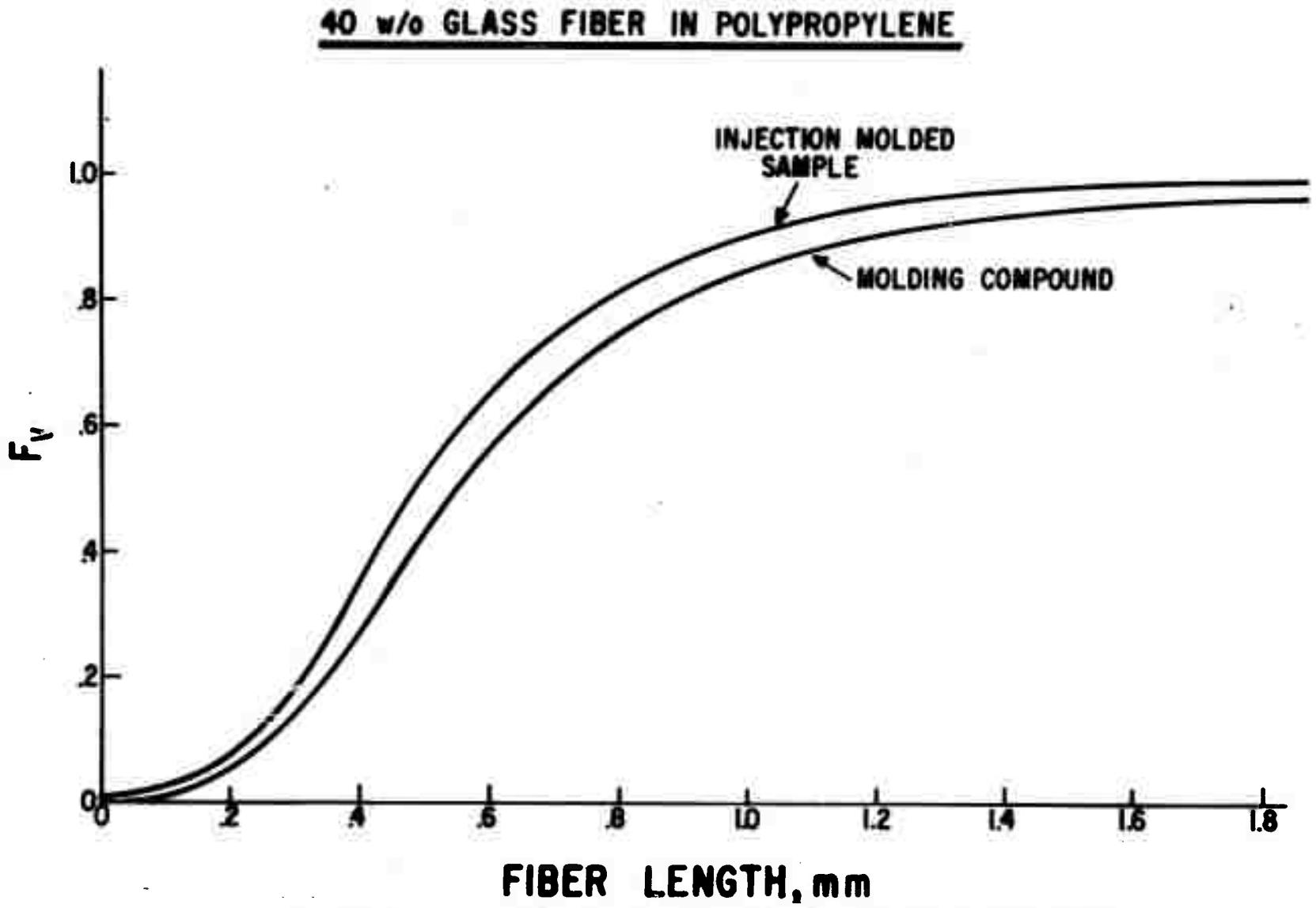


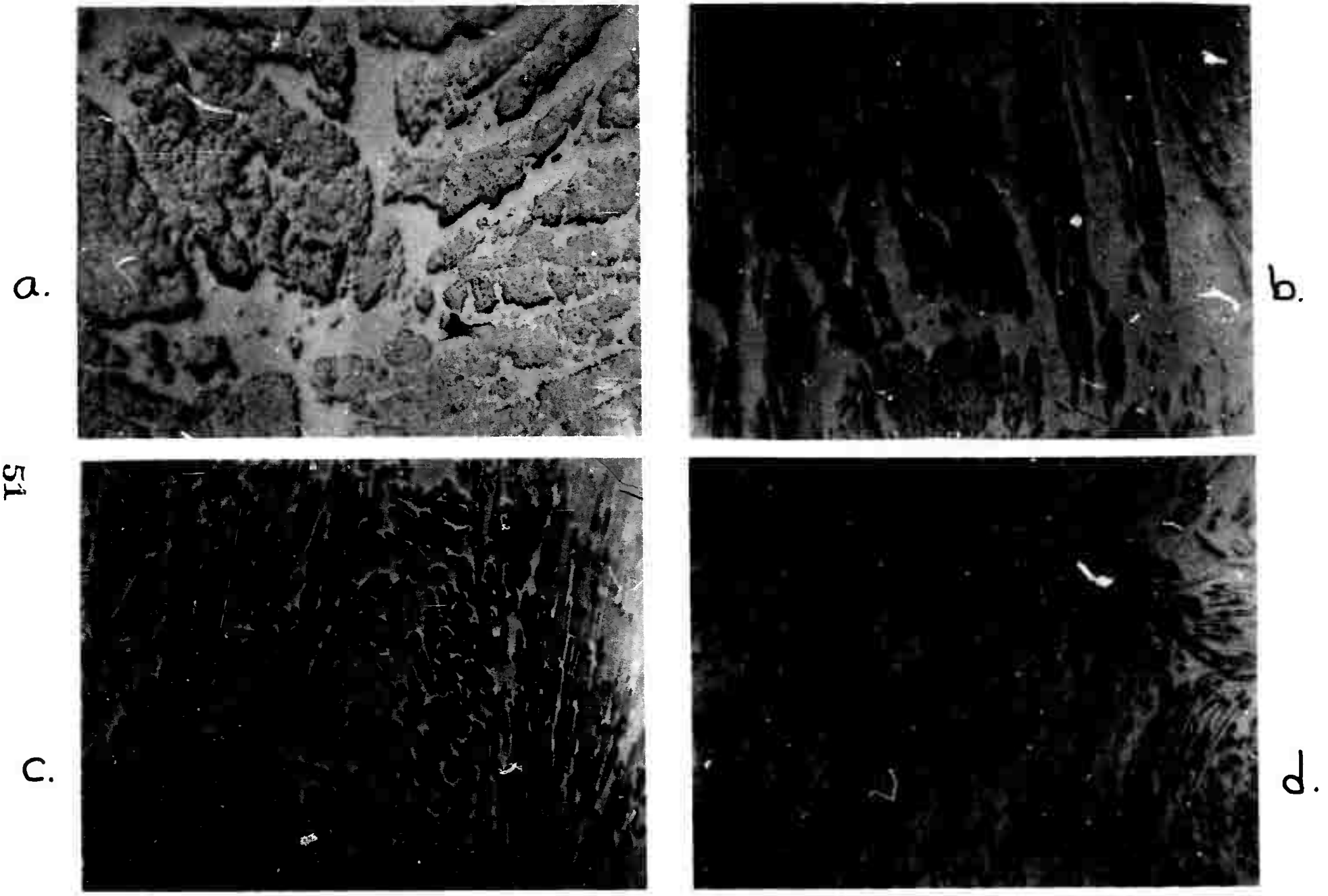
6. Fiber length distribution in fiber reinforced thermoset moldings.



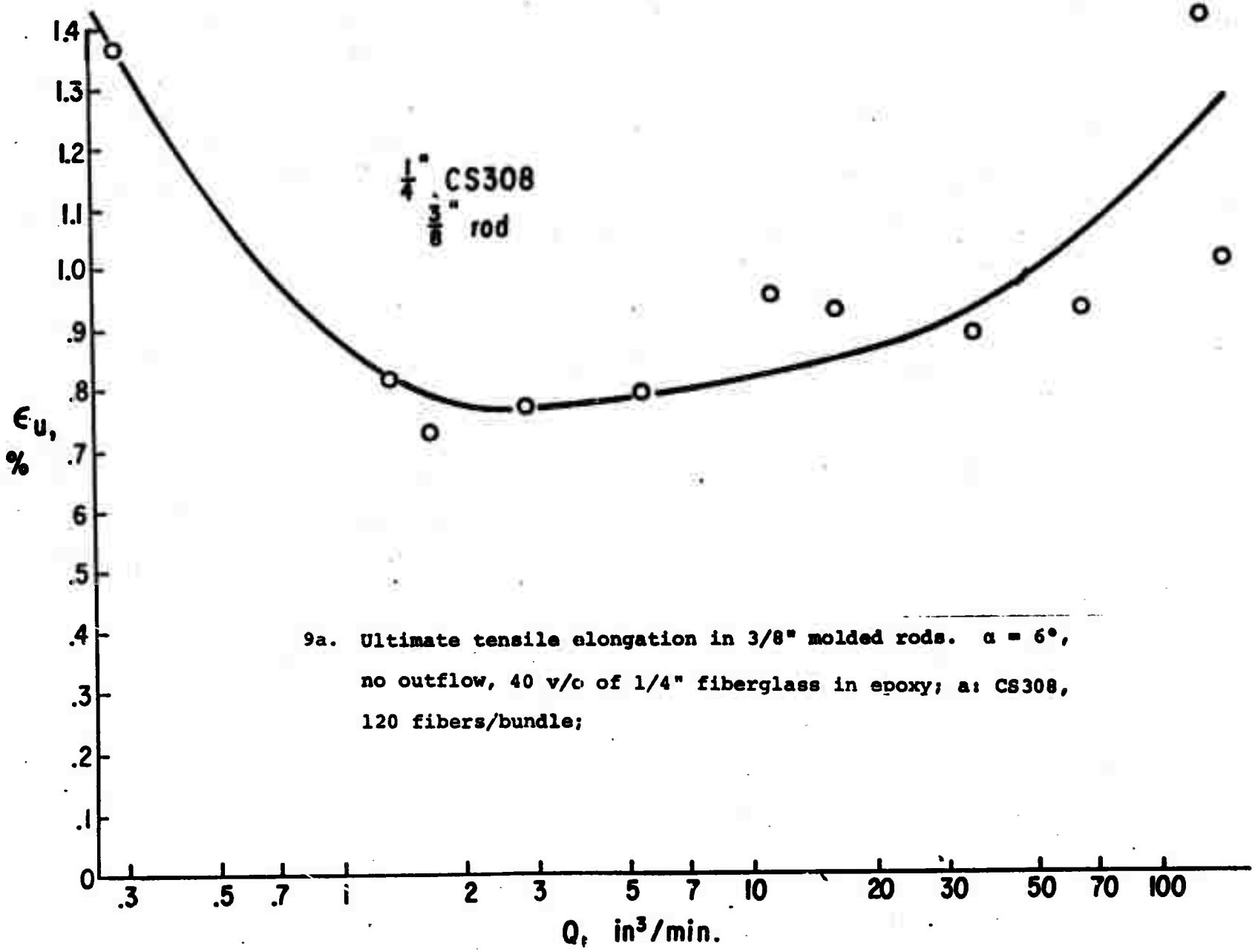
7a. Fiber length distribution in fiber reinforced thermoplastic moldings; a: polypropylene.



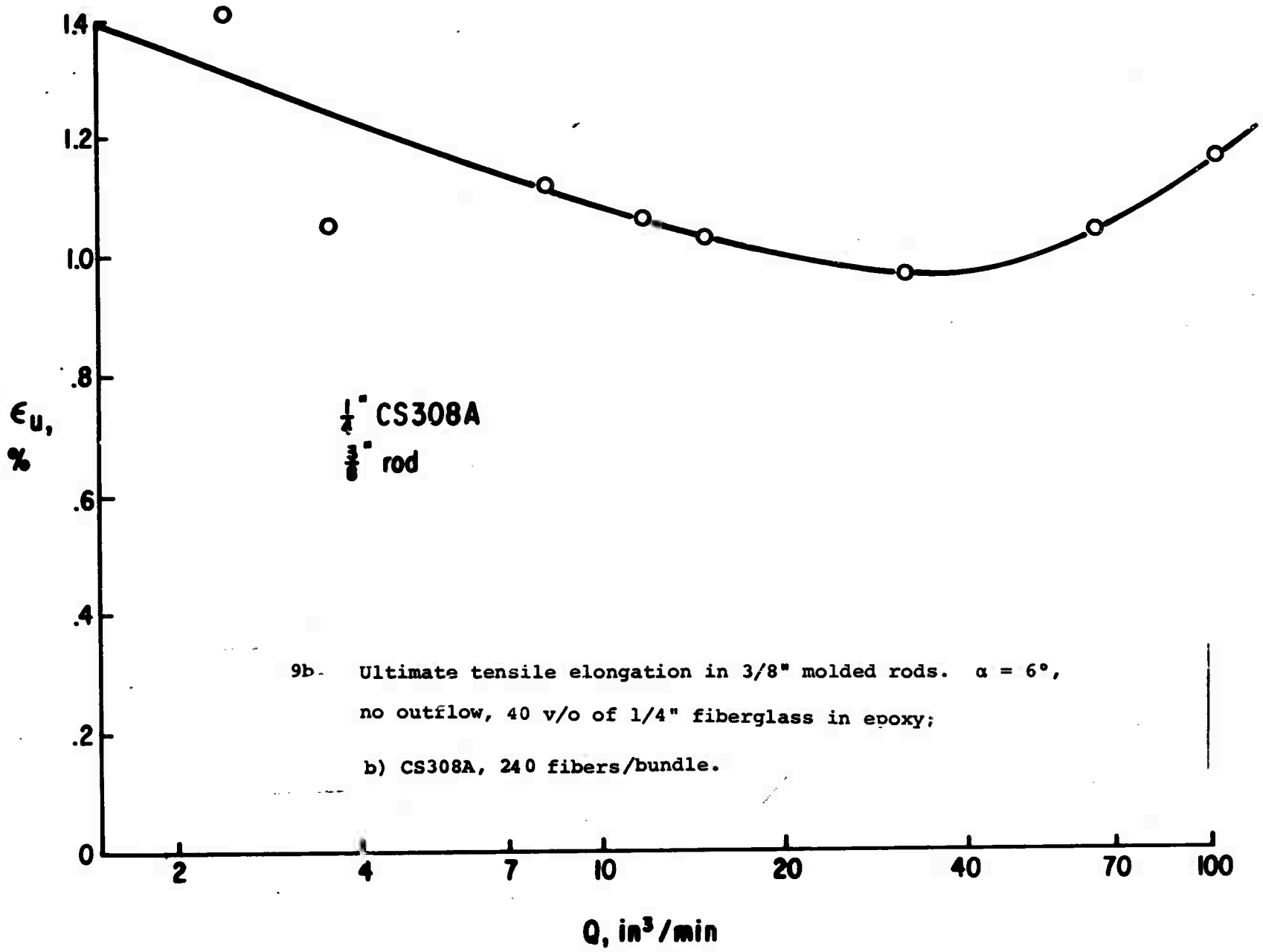
7b. Fiber length distribution in fiber reinforced thermoplastic moldings; b: nylon 6.



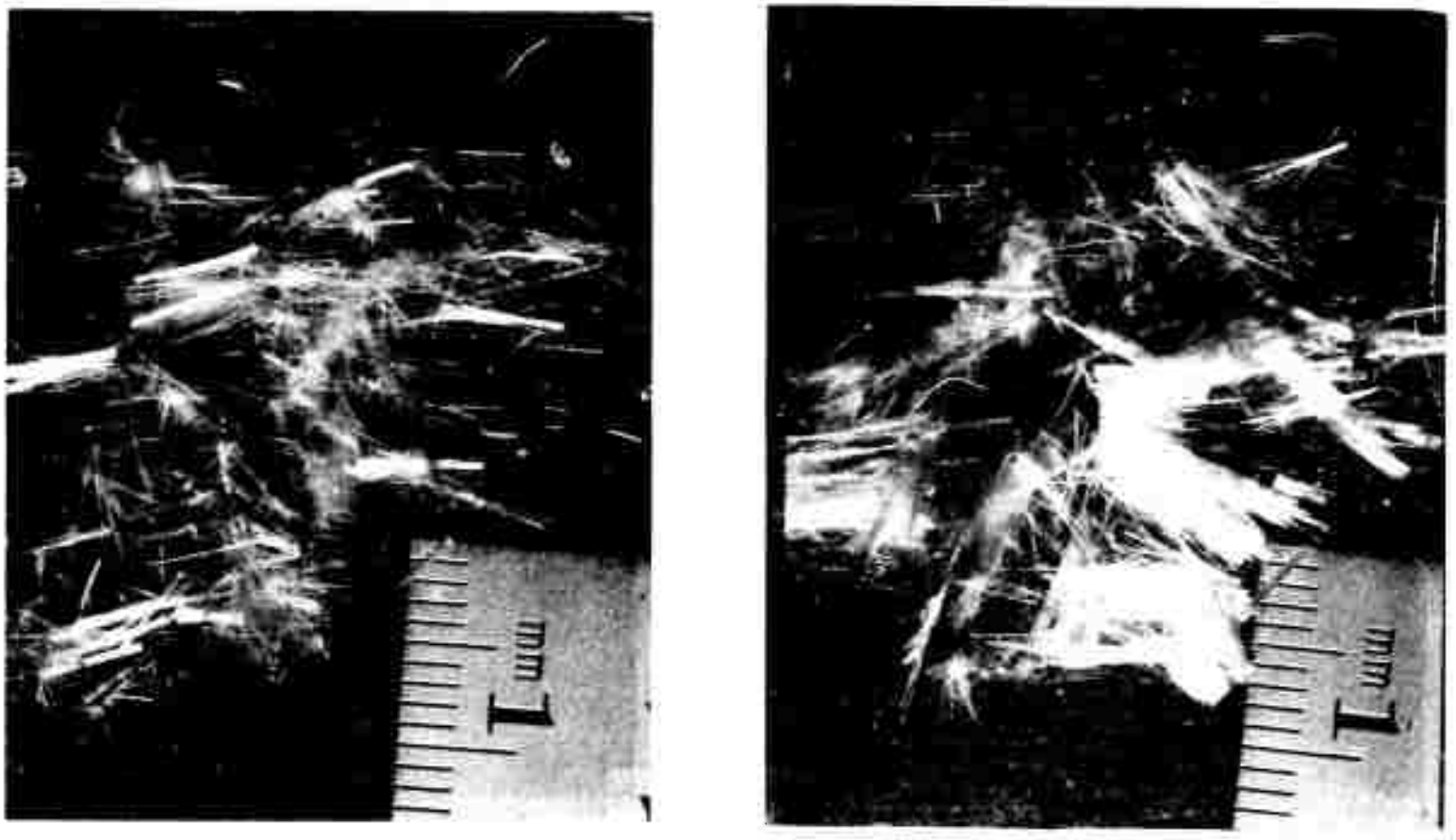
8. Fiber bundle disintegration during flow through a 1/2" x 1/8" runner; slow flow of 40 v/o 1/8" CS308A fiberglass in epoxy.



9a. Ultimate tensile elongation in 3/8" molded rods. $\alpha = 6°$, no outflow, 40 v/o of 1/4" fiberglass in epoxy; a: CS308, 120 fibers/bundle;



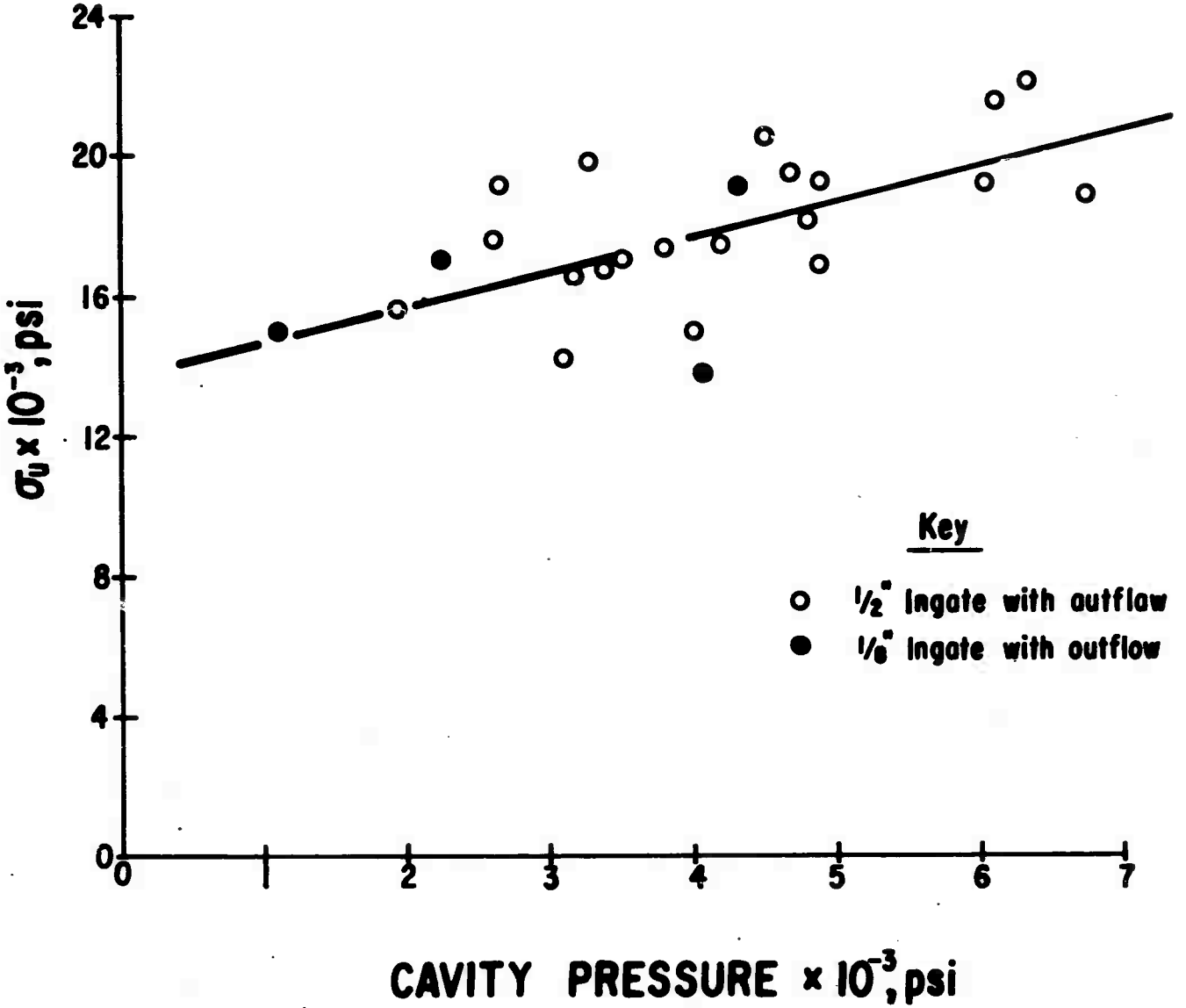
9b. Ultimate tensile elongation in 3/8" molded rods. $\alpha = 6°$, no outflow, 40 v/o of 1/4" fiberglass in epoxy; b) CS308A, 240 fibers/bundle.



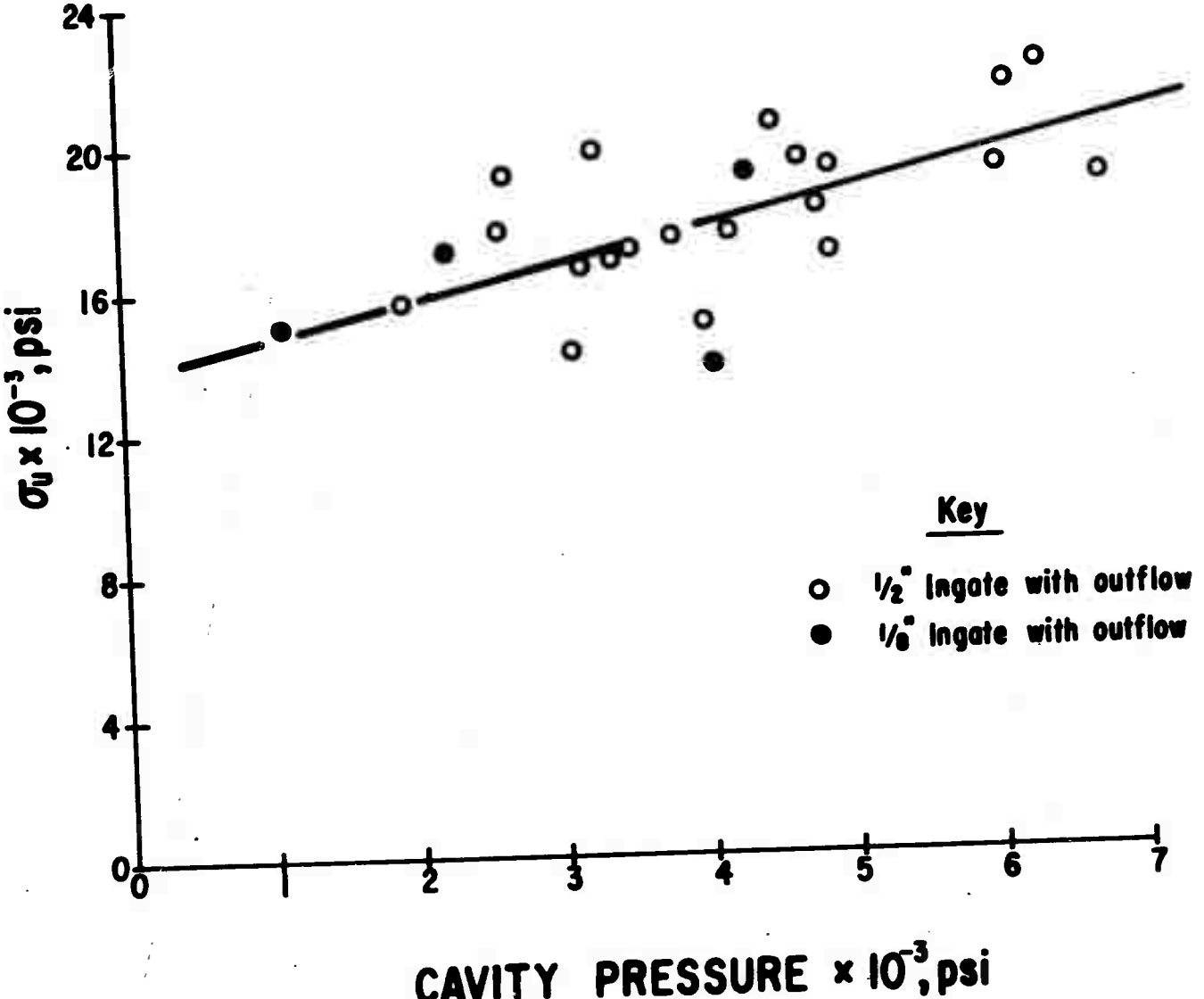
10. Fiber dispersion in 3/8" molded rods; $\alpha = 6°$, 40 v/o of 1/4" CS308 in epoxy; a: $Q = 2.9$ in^3/min; b: $Q = 146$ in^3/min.

11. Transverse elongated void in an end-gated bar of epoxy reinforced with 40 v/o of 1/8" CS308A fiberglass.

12. Microvoids resulting from incomplete fiber wet-out in an epoxy reinforced with 40 v/o of 1/8" CS308A fiberglass.



13. Tensile strength increasing with mold pressure; 40 v/o 1/8" CS308A fiberglass in epoxy; 1/2" rod ($A°/A = 6.25$), $\alpha = 6°$.



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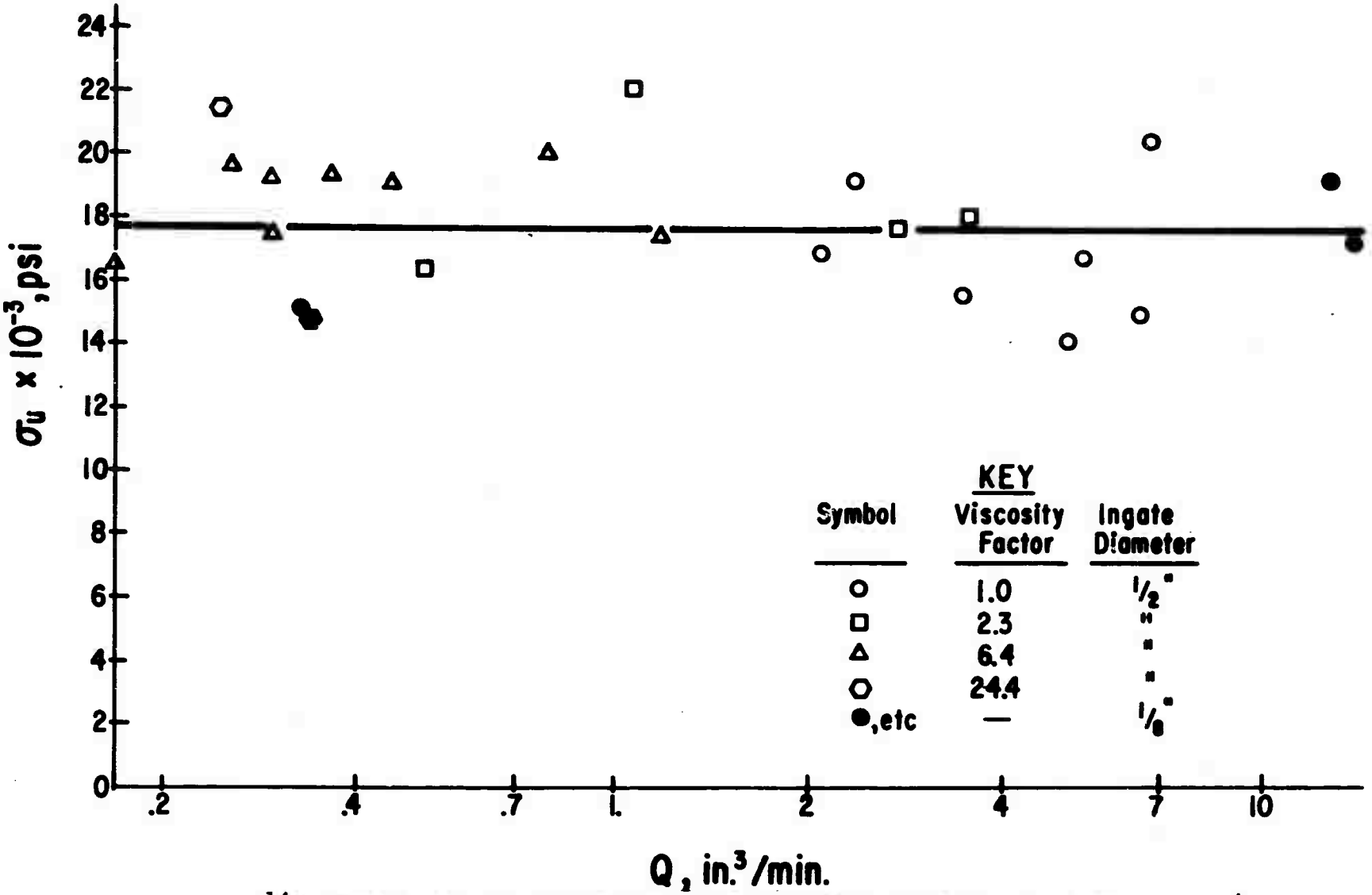
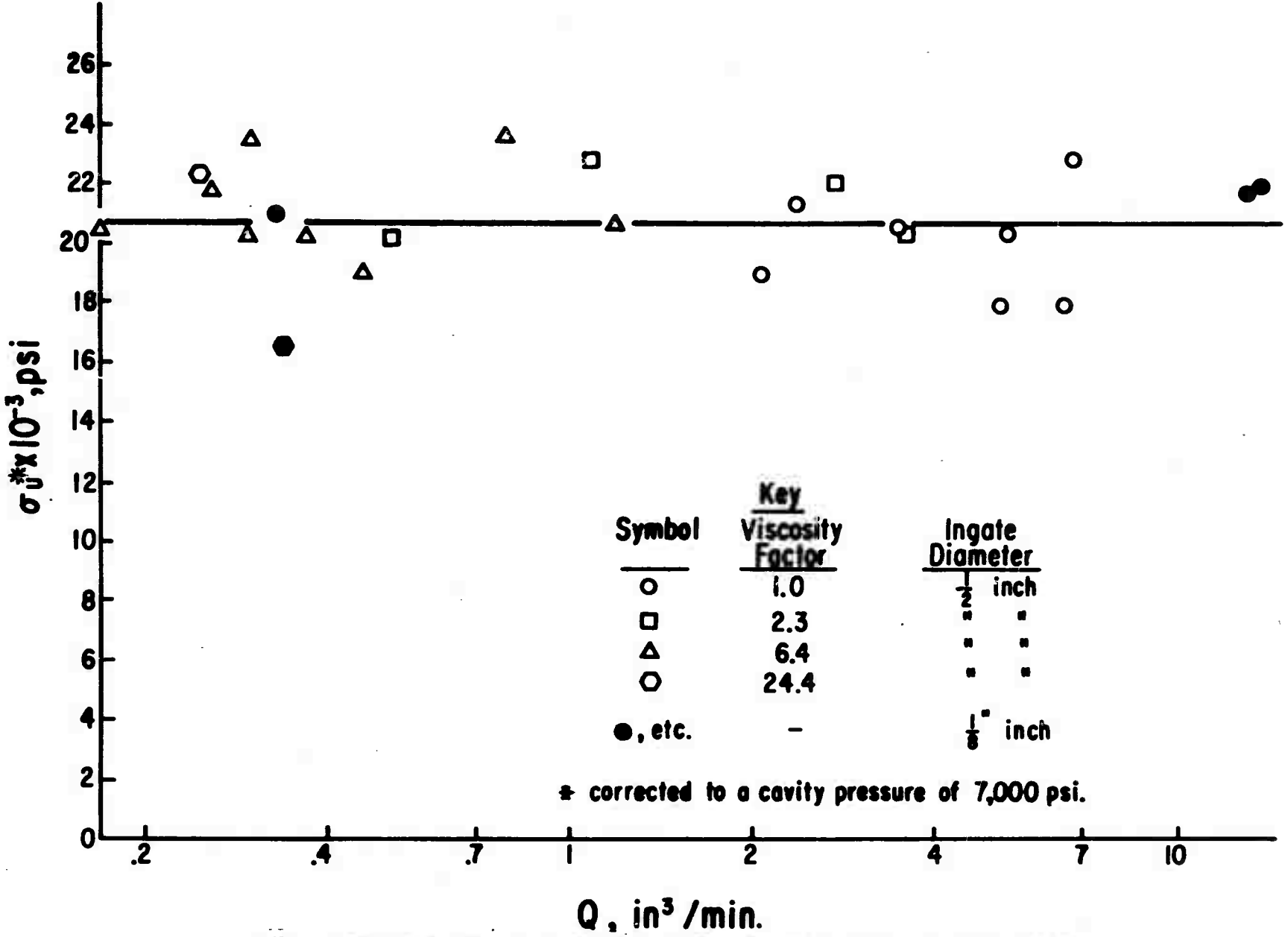
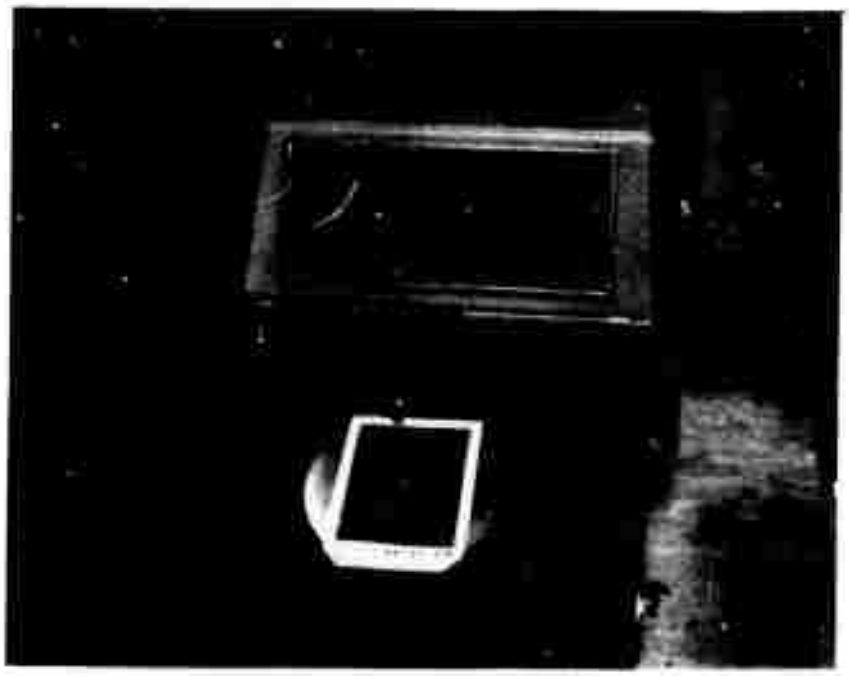


14a. Tensile strength of molded rods over variations in fill rate, viscosity and gating; 40 v/o 1/8" CS308A fiberglass in epoxy; 1/2" rod (A°/A = 6.25), α = 6°: a) as measured; b)



14b. Tensile strength of molded rods over variations in fill rate, viscosity and gating; 40 v/o 1/8" CS308A fiberglass in epoxy; 1/2" rod ($A^\circ/A = 6.25$), $\alpha = 6^\circ$: b) corrected to 7,000 psi cavity pressure by linear interpolation.



A-1. Zeiss particle size analyzer.

A-2. A distribution of fibers ready to be measured.